UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

DATE 16 NOV 1979

SUBJECT PP#s 9F2203/9F2213: Metolachlor in Potatoes and Peanuts. Evaluation of Residue Data and Analytical Method

FROM Alfred Smith, Chemist, RCB, HED (TS-769)

TO PM# 23 (Willa Garner), RD (TS-767) and TOX, HED (TS-769)

THRU: Chief, Residue Chemistry Branch TS-769 DC.

The CIBA-GEIGY Corporation proposes tolerances for combined residues of the herbicide metolachlor, {2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide}, and its metabolites determined as (2-{(2-ethyl-6-methylphenyl)amino}-1-propanol) and (4-{2-ethyl-6-methylphenyl}-2-hydroxy-5-methyl-3-morpholinone), each expressed as metolachlor, as follows:

PP# 9F2203

0.1 ppm	Potatoes

PP# 9F2213

0.1 ppm	Peanuts
1.0 ppm	Peanut hulls
3.0 ppm	Peanut forage and hay

Permanent tolerances are established for metolachlor in corn grain (except popcorn) at 0.1 ppm; soybeans at 0.1 ppm, and eggs, milk, and the meat, fat, and meat byproducts of livestock at 0.02 ppm (§180.368).

Conclusions

1. The nature of the residue in animals and peanuts is adequately understood. The absence of a potato metabolism study precludes valid conclusions on the nature of the residue in potatoes. Metabolism studies for potatoes are needed and should be submitted.

2. Adequate analytical methods are available for the tolerance on peanuts for enforcement purposes. Because the nature of the residue in potatoes is not known, we cannot determine if the analytical method is applicable to potato residues.

3(a) Residues of metolachlor in or on peanuts and its byproducts (meal, oil, soapstock), peanut hulls, and peanut forage and hay are not likely to exceed the proposed tolerances. The absence of potato metabolism studies precludes valid conclusions on residues in potatoes.

3(b) Residues of metribuizin in potatoes are not likely to exceed the established tolerance (0.6 ppm) due to the tank-mix use.

3(c) Residues of alanap or dinoseb in or on peanuts and its byproducts, peanut hulls, and peanut forage and hay are not likely to exceed the established tolerances due to use following metolachlor treatments.

4. Residues of metolachlor could occur in eggs, milk, and meat of livestock due to the use on peanuts.{§180.6(a)(2)}. However, such residues would be adequately covered by the established tolerances. The absence of adequate residue data for potatoes precludes valid conclusions on metolachor residues in eggs, milk, and meat due to the use of metolachlor on potatoes.

Recommendations

Toxicological considerations permitting, we recommend for the proposed tolerances for peanuts. We recommend against the proposed potato tolerance due to deficiencies noted in Conclusions 1,2,3(a), and 4.

Detailed Considerations

Proposed Uses

Metolachlor, formulated as Dual 6E (6 lb. act./gal) and Dual 8E (8 lb. act./gal), is proposed for aerial or ground use as a preplant or postplant incorporated, or pre-emergence application for grass and weed control in potatoes and peanuts.

Potatoes

Apply metolachlor alone before emergence of crop and weeds or after final drag-off at rates of 1-3 lb act/A depending on the soil type. An interval of 70 days from last treatment to harvest (PHI) is proposed.

The formulation is not to be used on sweet potatoes or yams.

Metolachlor and *metribuzin is proposed as a tank-mix use at rates of 1.5-2.5 lb metolachlor/A + 0.38-0.75 lb. metribuzin/A.

The tank-mix is not to be used on potatoes in Kern County, California, and it is not to be applied to sweet potatoes or yams. In a conversation with Mr. Jack Norton (Ciba-Geigy Corp) on 10/31/79, we were informed that the Kern County restriction has been imposed because of phytotoxicity problems. The same restriction appears on metribuzin labels.

*Metribuzin (Sencor) is registered for pre-or postplant or preemergence application on potatoes with a maximum application of 1.0 lb. act/A in any single crop season with a 60-day PHI. Metribuzin is not to be applied to sweet potatoes or yams. A tolerance of 0.6 is established on potatoes.

Peanuts

Apply metolachlor alone before emergence of crops and weeds at rates of 1.5-3.0 lb. act/A depending upon the soil type.

Metolachlor may be applied as above and followed with an application of Dyanap(R) at preemergence to cracking time at 4.5 lb. act/A(3 lb. alanap/ 1.5 lb DNBP).

Dyanap(R) contains 22.3% sodium N-1-naphthyl phthalamate (alanap) and 11.5% sodium salt of dinoseb (2,4-dinitro-6-sec-butylphenol;herbicide/ insecticide/desiccant). Dyanap(R) is a 2:1 mixture of alanap and dinoseb.

Alanap is registered for use on peanuts at 8.0 lb. act/A (preemergence immediately after seeding) and 3.0 lb. act/A at cracking time (5-7 days after planting) to first true leaves. Alanap has an established tolerance of 0.1 ppm in peanuts and hay.

Dinoseb (DNBP) is registered for use (as the alkanolamine salts of the ethanol and isopropanol series) on peanuts at rates of 1.5-12.0 lb. act/A for preemergence and postemergence applications. A tolerance of 0.1 ppm is established for peanuts, peanut forage, and peanut hay.

The formulations' inert ingredients are cleared for use under §180.1001. The manufacturing process and the composition of technical metolachlor are discussed in PP# 8F2081. The impurities are not likely to produce a residue problem.

We have considered the question of the possible presence of nitrosoamines in previous memos (PP# 7F 1913). We concluded that nitrosoamine formation is unlikely.

Nature of the Residue

We have considered the metabolism of metolachlor in plants and animals in previous reviews (PP# 7F1913, 6G1708, 6F1606, 5G1553). Plants (corn, soybeans) absorb, translocate, and metabolize metolachlor. The primary path of plant metabolism involves hydrolysis and conjugation with plant constituents.

There are no metabolism studies for the root crop potatoes, nor are there studies for any root crop. A metabolism study is needed to show the nature of the residue for root crops.

Metolachlor is ingested, metabolized, and rapidly eliminated by animals (rats, goats, cattle, chickens) with some deposition of residues in tissues. While the conjugating natural components in animals differ from those in plants, the metabolic components are similar.

The nature of the residue in corn, soybeans and animals is similar. The significant components of the residue consist of the parent compound and its metabolites: 2-(2-ethyl-6-methyl phenyl)amino)-1-propanol; and, 4-(2-ethyl-6-methylphenyl)-2-hydroxy-5-methyl-3-morpholinone). The analytical method determines these components and their conjugates.

The nature of the residue is adequately delineated for peanuts and animals.

Analytical Methods

Metolachlor: a sample is refluxed overnight with dilute hydrochloric acid. (This procedure converts metolachlor, its metabolites, and conjugates to CGA-37913 and CGA-49751). The extract is made basic, and the CGA-37913 is extracted into hexane. This extract is cleaned up on an alumina column and concentrated. The CGA-37913 in the concentrate is determined by gas-liquid chromatography (GLC) using an electrolytic conductivity detector which is sensitive to nitrogen. The results are expressed as ppm metolachlor (method AG-265).

For CGA-49751, the initial sample hydrolysis with dilute hydrochloric acid is as above. The acid extract is partitioned with dichloromethane which separates CGA-49751 and CGA-37913. The dichloromethane phase containing CGA-49751 is washed with a dilute sodium carbonate solution, converted to the chloroethanol derivative by reaction with boron trichloride/2-chloroethanol. The derivative is extracted into hexane, and an aliquot of the extract is cleaned up on a silica gel column followed by an alumina column. The eluate is concentrated, and the CGA-49751 is determined as above. The results are expressed as ppm metolachlor (method AG-286).

Untreated (control) samples of peanut meal, oil, and soapstock, and potatoes, peanuts, and peanut forage, hay and shells had metolachlor equivalent residues of <0.01-0.11 ppm. Control samples, fortified at levels of 0.02-0.50 ppm, had recoveries of 36-118%.

The Method AG-286 has been successfully tested with metolachlor and its metabolites on corn grain and meat. We believe the results of the trials can be extended to include potatoes, peanuts, and its byproducts, and peanut forage, haym and shells. Adequate analytical methods for use on peanuts are available for enforcement purposes.

Because the nature of the residue in potatoes is not known, we cannot determine if the analytical methods are applicable to potatoes.

Metribuzin: the procedure is included in "Analytical Methods for Pesticides and Growth Regulators, Vol. VIII, G. Zweig and J. Sherma, Ed. 1976." A ground sample is refluxed with acetonitrile/water to release metribuzin and conjugated metabolites. The acetonitrile is evaporated, and the residues are extracted into chloroform, which is then extracted with sodium hydroxide. Metribuzin remains in the cloroform phase and the metabolites partition into the aqueous phase.

The aqueous phase is acidified, extracted with chloroform, and evaporated to dryness. The chloroform phase containing metribuzin is cleaned up on a Florisil column and eluted. The metabolites' phase is cleaned up with a silica gel column and eluted.

The residues in the eluates are determined by gas chromatography using an electron capture detector. The method is similar to the method used for analyses of soybeans (PP# 8F2081). The method for soybeans has been successfully tested on soybeans by EPA and is included in PAM II as method I.

Residue Data

Peanuts

Samples were obtained from crops in North Carolina, Georgia, Texas, Virginia, and Oklahoma. The crops had been treated as proposed at 1x and 2x the maximum proposed rates. The nutmeats had no detectable residues (NDR, <0.05 ppm) at PHIs of 128-159 days from the 1x rate. Residues due to the exaggerated 2x rate were <0.05-0.15 ppm in nutmeats at PHIs of 146 days and 159 days.

The hulls had residues of 0.14-0.68 ppm from the 1x rate at PHIs of 128-159 days. Residues due to the 2x rate were 0.22-2.04 ppm during the same PHIs.

The forage had residues of 0.21-2.27 ppm from the 1x rate at PHIs of 56-69 days. At the 2x rate residues were 0.26-3.63 ppm ppm during the same PHIs.

The hay had residues of 0.52-2.60 ppm due to the 1x rate at PHIs of 128-159 days. At the 2x rate, residues were 0.87-5.60 ppm for the same PHIs.

Peanut byproducts

Nutmeats which had residues of 0.05-0.07 ppm were processed, and the byproducts were analyzed for metolachlor residues. No concentration of residues were noted. The byproducts had the following levels: meal (<0.05-0.07 ppm); oil (<0.05 ppm); soapstock (<0.05 ppm).

We conclude that residues of metolachlor in peanuts or its byproducts, peanuts hulls, peanut forage, or hay are not likely to exceed the proposed tolerances from the proposed uses.

Sequential treatments No data were submitted in which crops were treated in sequence as proposed. However, data were submitted in which crops were tested in sequence as proposed. However, data were submitted in which crops were treated with metolachlor in combination with the Dyanap 3E formulation. No analyses for either alanap or dinoseb were performed; however, a comparision of the metolachlor residue levels resulting from treatments with metolachlor alone or in combination with Dyanap 3E (alanap + dinoseb) showed no significant differences in metolachlor residue levels for the two treatments.

Since no significant differences were noted in metolachlor residue levels for the combination treatment, it is not likely that either metolachlor residue levels, alanap residue levels, or dinoseb residue levels would be significantly affected by the proposed sequential treatment (metolachlor followed by Dyanap 3E). Furthermore, the registered rated for alanap and dinoseb are 2.7x and 7x, respectively, the proposed sequential rates.

In view of the foregoing, we conclude that residues of metolachlor are not likely to exceed the proposed tolerances in peanuts, or its by-products, hulls, forage, or hay due to the proposed sequential treatment Additionally, residues of alanap or dinoseb are not likely to exceed the established tolerances in peanuts, peanut forage, and peanut hay.

Potatoes

Metolachlor alone - samples were obtained from crops in California, Mississippi, Washington, and New York which had been treated as proposed at the maximum proposed rate of 3 lb. act/A and an exaggerated rate of 6 lb act/A. Residues in potatoes from 3 lb. act/A were <0.08-0.12 ppm at intervals of 48-60 days after treatment (PHI); <0.08-0.09 ppm at 60-67 days, and <0.08 ppm (no detectable residues, NDR) at 71 days and beyond.

Residues due to the 6 lb. act./A rate were <0.08-0.50 ppm at 48-58 days, and < 0.08-0.11 ppm at 60 days and beyond.

Tank-Mix Use - samples were obtained from crops in Florida, Mississippi, Pennsylvania, Washington, and Minnesota which had been treated as proposed at the proposed rates. No detectable residues of either metolachlor (<0.08 ppm) or metribuzin (< 0.2 ppm) were noted in potatoes at PHIs of 48-135 days.

Residues of metribuzin, if any, in potatoes from the tank-mix use would be adequately covered by the established potato tolerance (0.6 ppm).

Since we have no information on the nature of the residue in a root crop, the metolachlor residue picture for potatoes may be different from that of non-root crops. As a result, we conclude that the absence of studies on the nature of the residue in root crops precludes valid conclusions on the residue level in potatoes.

Meat, Milk, and Eggs

Potatoes, peanuts, peanut meal, peanut oil, soapstock, peanut vines, hay, and hulls are used as livestock feeds in varying amounts. Considering the percentages usually fed, the livestock will ingest the following maximum levels of metolachlor residues: cattle (1.8 ppm); poultry (0.02 ppm); swine (0.3 ppm); horses (0.25 ppm); sheep and goats (0.75 ppm). These levels include the feed item potatoes and assume a residue picture similar to peanuts which may not be the case. The maximum levels are therefore exaggerated.

Permanent tolerances are established at 0.02 ppm in eggs, milk, meat, fat, and meat byproducts of livestock. The tolerances are supported by livestock feeding studies in which dairy cows and goats were fed metolachlor residues at levels of 0-5 ppm and laying hens were fed at levels of 0-2 ppm (see also PP# 7F1913). In view of the maximum ingestion levels indicated above, we conclude that any metolachlor residues which might occur in eggs, milk, or meat due to the feed use of peanuts would be adequately covered by the established tolerance {§180.6(a)(2)}.

The absence of adequate residue data for potatoes precludes valid conclusions on metolachlor residues in eggs, milk, and meat due to the feed use of metolachlor treated potatoes.

Alfred Smith

Alfred Smith